AD 668910

Best Available Copy
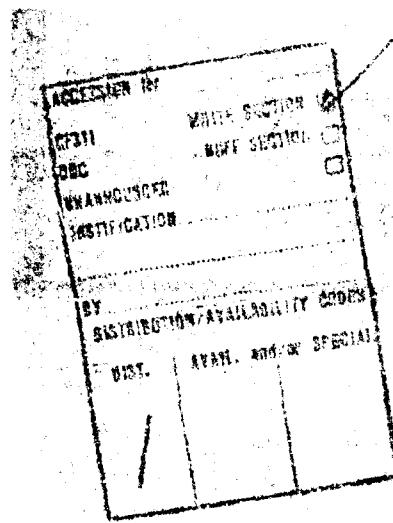
This document has been approved for public release and its distribution is unlimited.

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of trade names in this report does not constitute an official indorsement or approval of the use of such items.

Destroy this report when no longer needed. Do not return it to the originator.

AD_____

TECHNICAL REPORT
68-45-CM

STRENGTH LOSSES IN NYLON PARACHUTE MATERIALS
WITH TIME, EXPOSURE, AND USE

by

Frank Figucia, Jr.
and
Richard D. Wells

March 1968

FOREWORD

Since there are no feasible means for detecting individually when personnel parachutes have degraded to levels of deficiency, reliability control has been managed by standard retirement formulas. Determination of these service life limits to satisfy both reliability and economic requirements is a problem with no exact solution. Limiting ages and number of jumps have been prescribed largely by user experience supplemented by tests on small samplings.

The studies on which this report is based were undertaken to provide additional data in guidance of limits for U. S. Army parachute types and usages, and to gain further insights into the extent and nature of the degradation problem. Particularly in question was the premise of the consistency and predictability of trends, which is the primary rationale for control by wholesale methods. Related questions concerned the validity of historical experience and spot surveys in assessing the conditions within the parachute populations at large.

The test projects and analyses were conducted under the Applications Engineering Task, "Safe Life Span of Personnel Parachutes in Service and Storage," within the Project "Aircraft Components and Accessories." Detailed findings are reported in Material Examination Reports as referenced.

S. J. KENNEDY
Director, Clothing & Organic
Materials Laboratory

APPROVED:

DALE H. SIELING, Ph.D.
Scientific Director

CLIFFORD T. RIORDAN
Colonel, QMC
Commanding

iii

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

The findings of recent U. S. Army Natick Laboratories tests
on aged and used nylon parachutes are reviewed with respect to
service life limits and to implications as to the technical
nature of the degradation problem. The data tend to confirm
that the current 10 year or 100 jump limits and related repair cost
limit schedules do not present a hazard. However, the scatter
and contrasts of results make questionable the validity of small
samplings and extended predictions. No consistent and pervasive
trends were found to be directly related to time in storage or
service, or to jump history except for initial mechanical effects
on suspension lines. The results evidenced marked differences
in the specific susceptibilities of various materials, and a
number of degrading influences and types of effects on physical
properties.

A wide distribution of strength levels is to be expected
in older parachute populations, and the risk problem is with
the exceptional cases rather than with the average condition.
A number of possible chemical structural change mechanisms are
discussed.

STRENGTH LOSSES IN NYLON PARACHUTE MATERIALS
WITH TIME, EXPOSURE, AND USE

I. Introduction

Nylon parachute materials are subject to strength losses and other
changes in performance properties because of age, environment,
contaminants, and use. This susceptibility is recognized in the
originally designed safety factors, and in the scheduled
retirement of old equipment. Decisions in these areas have had
to be made with rather meager data. Service life limits are
prescribed in terms of age from date of manufacture (now
variously 7 to 10 years), number of jumps (100), and as
indirectly applied in the "excessive" repair cost formula used
for troop main parachutes. For repair materials, 5 years is the
current limit. Limits as short as 6 months from date of
installation are set for certain components of ejection seat
systems.

These practices have been successful in the sense that no
actual service failures of personnel parachutes have been
attributed to strength deficiencies of the materials when used
under normal circumstances. However, questions are continually
raised as to how satisfactory the current methods actually are
in terms of the risk-cost equation.

Each of the military services has had projects to assess
the condition of the older parachute equipment. Though broader
investigations were proposed,[1,2] the authorized efforts were
limited to spot surveys intended to provide data in support of
then prescribed age or jump limits or possibly a basis of
assurance for further extensions. These individual tests yielded
no distinct evidence of imminent hazard and gave no convincing
support to proposals for extensions. The decision in 1959 to
extend the Army parachute service life limit from 7 to 10 years
was based largely on field judgment. Results of subsequent
test projects have not changed this decision.

However, as successive projects were completed, it became
increasingly apparent that the spot surveys were probably
yielding only fragmentary evidences of a complex situation.

The present study was undertaken to consider the collective data for broader implications of the nature and extent of the problem, in guidance of future policies and programs. With the marked strength losses which occasionally appear, and knowledge of what can occur under certain possible circumstances, it is apparent that the problem of maintaining full reliability within the parachute population warrants more concerted attention. Newer concepts of air deployment of troops will impose more rigorous demands on material performance and reliability. Additional justification is in the proper management of nylon materials in cargo aerial delivery systems (both drop and suspended) and in drogue and arrestor equipment which are not currently under service life limitations. Also, there is a growing number of other critical applications for nylon and other synthetic fibers within the millitary system.

II. General Commentary

A. Reliability and Cost

For personnel parachutes, no compromise is knowingly made with reliability. However, there should be full assurance that reliability is, in fact, being maintained. Also, there should be no clearly unnecessary costs incurred in realizing that objective.

With respect to reliance on historical experience as the primary assessment of performance reliability, it is first to be recognized that the proportional sampling comprised of the few reserve and emergency parachutes ever actually used is very small. Also, it must be recognized that the used units would have been from any of the age classes on hand; there was no way of determining how marginal their performance had been, and the conditions of use may have been well within the designed performance envelopes. Consequently, past experience is even less a measure of the true capability of older equipment. Since the spot surveys were also very limited and rather arbitrary in sampling, there is currently no firm basis for confidence that the intended reliability is being or will be maintained under present service life limits.

The assessment of older age classes of parachutes used in premeditated jumps is a special case since nearly all units have been discarded according to "excessive" repair cost formula based on attained age or jump history, well before reaching the prescribed overall limits. Consequently, this historical experience provides no basis for predicting the reliability if conditions of supply and operations changed so that more of the older parachutes did remain in the system.

2
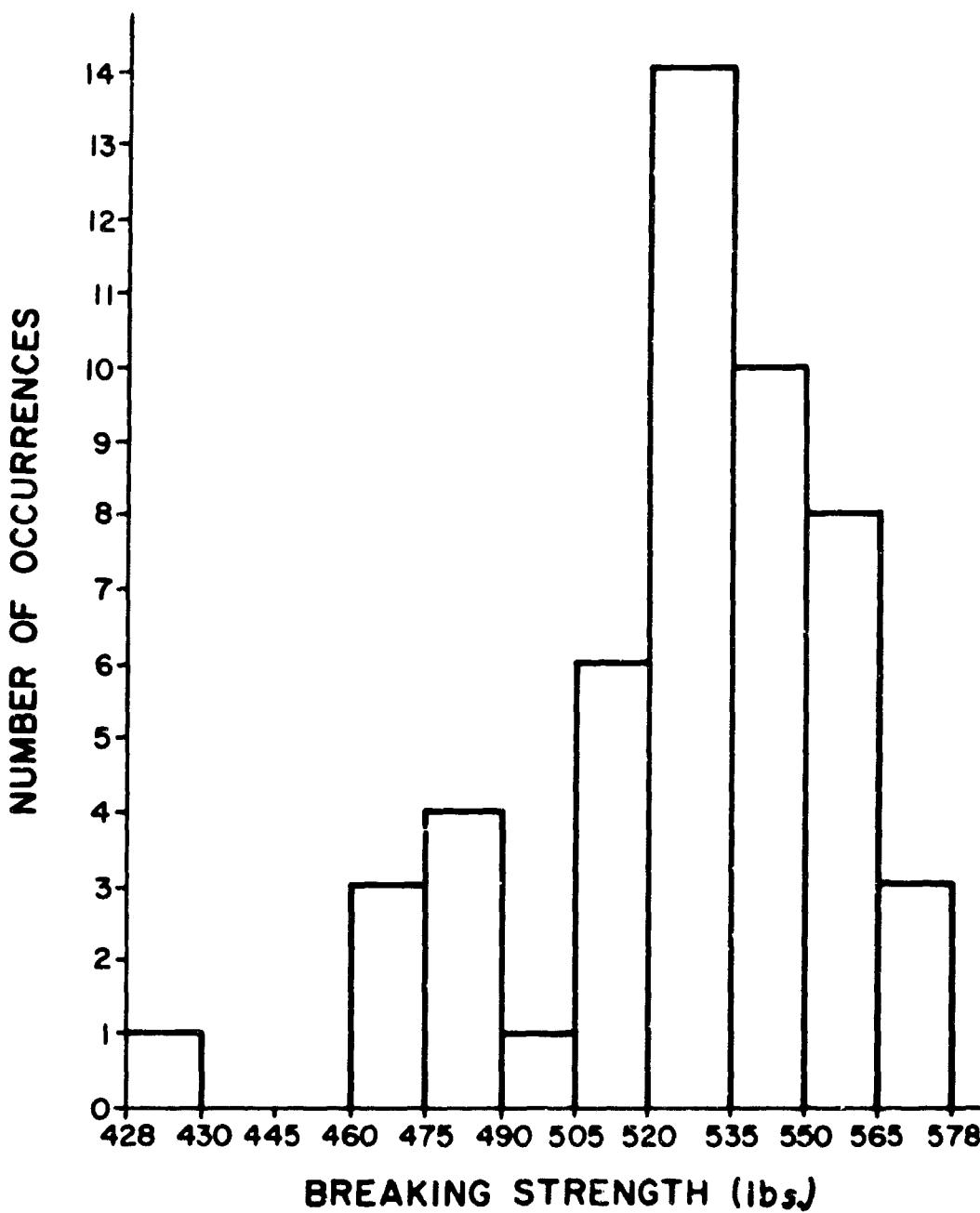
FREQUENCY DISTRIBUTION OF SUSPENSION LINE STRENGTH
RESULTS FROM AGED RESERVE PARACHUTES

FIG. I

4

The two more obviously unsatisfactory aspects of the present system are in the cost, and that in times of peak demand there is actual shortage of equipment in service status. In the wholesale process to eliminate the small proportion of units believed to be nearing a deficient condition, a much greater number of parachutes are discarded while still having a considerable number of years of potential further service. Estimates of replacement costs solely attributable to premature retirements vary according to assumptions of losses and discards for other reasons, and to the years used as the experience base. A minimum of 5 million dollars has been taken as a potential saving (DoD) for each year the service life limits for personnel parachutes might be extended. In another view, it is estimated that the average annual cost of the unrealized unit-years of potential service is approximately 2 million dollars. This order of magnitude is too large to ignore, and also is restrictive to the build-up of emergency reserves.

A perspective on the economic and risk factors may be gained in the distribution of some of the test data. Figure 1 shows suspension line strengths in a sampling of 10 Type 7A reserve parachut ' of approximately 10 years of age. Figure 2 shows canopy fabric strengths of samples taken from 140 Type C-9 emergency parachutes of 7 to 9 years of age. From the high proportion of specimens in the normal strength range it may be reasonably concluded that most of the equipment of similar age and service history is still in quite good condition. However, the few values which are appreciably below that range must be considered in all their possible implications. With the variety of environmental and service circumstances which might have been encountered by other units within the age classes from which these samples were drawn, any prediction of the most extreme case, or of frequency of cases below some critical minimum strength, would be on very dubious grounds. In fact, such predictions for all individual lines and panels even within these sample groups could not be made with desired confidence.

B. Premises

The major difference between earlier and present assumptions is in the ranges and patterns of retained strength values to be expected. The problem can be assessed under normal statistical concepts only under the combined conditions that the original materials are uniform in their original properties and susceptibility, the deterioration process is simple and

3
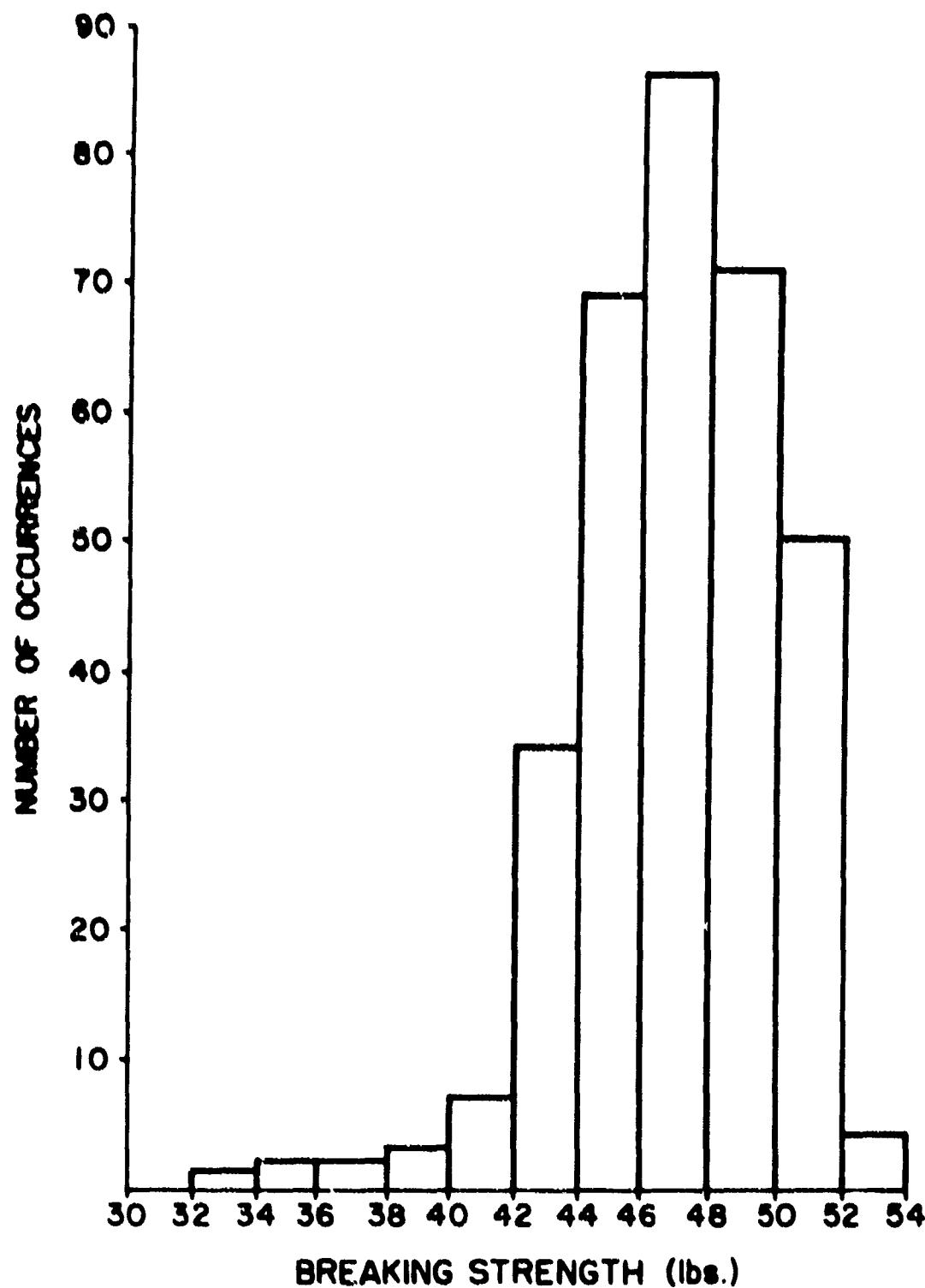
Frequency Distribution of Cloth Breaking Strength
Results from 140 Emergency Parachutes
Fig. 2

consistent, and the range of causative circumstances is narrow and their effects largely time-dependent. If, however, there is marked variance in any of these conditions, and the interactions are rather specific, then only very extensive and rigorous evaluations can provide confidence that the full situation is known and under appropriate control.

Though not explicitly stated, the original studies have been weighted by the concept that age, in the sense of elapsed time only, is a direct and important degradative factor. While specific external causes of degradation were well known, the idea of basic time-instability of the nylon materials as a common underlying cause of observed strength losses tended to the expectation of a general basic trend with a fairly narrow range of variation due to minor differences in rates and superimposed circumstances. Though subsequent test reports[3,4] rather denied that age, per se, is a serious factor, the idea was not fully refuted.

The conviction that ultraviolet (u-v) exposure is the predominating external factor[4,5] also supported the concept of a fairly uniform trend. Since the exposures are confined to regularly scheduled inspections, repacks and training jumps, and the exposure increments are small and distributed through a number of years, the cumulative effects would be largely averaged out within any type and age class. Presumably the frequency of more accidental and exceptional cases would be low and most of the affected units would be detected by the obviousness of the circumstance or the degradation, or by associated evidences such as discoloration.

The cumulative picture revealed by the U. S. Army "safe-life" limit studies and related U. S. Navy and Air Force investigations[6] does partially substantiate that a slow general trend of changes in the nylon properties is to be anticipated. It is reasonable to assume that this trend is attributable to u-v exposures and common contact and atmospheric contaminants encountered in service, and possibly to inherent instability and oxidative effects also affecting equipment in storage. But this general trend is apparently very slow. If the predominating body of data is taken at face value under the assumption of consistent conditions and degrading processes, and the original safety factors were as large as planned, then appreciable extensions beyond present service life limits might appear to be warranted

6

However, with the diversity and seeming anomalies in the collective data, the view of the problem as a dominant and universal trend with minor variations cannot be supported. What appears in some instances to be a consistent pattern may reflect only a particular sub-group, or a variety of change phenomena which the test programs were not designed to distinguish. Since the more serious practical problem is now seen to be the extreme deviations rather than the common trend, the present discussion emphasizes the differences more than the average or "typical" case.

C. Types of Degradation

The term degradation has been used rather broadly to indicate any unfavorable changes in mechanical properties of the materials. The processes which result in these changes include some that are truly deteriorative in breakdown of the basic polymeric chains. Evidences of such breakdown are frequently found in "degraded" materials from service. Since they are also commonly found in accelerated exposures to u-v, oxygen, heat, and acids in laboratory studies, there has been a prevalent tendency to assume that chain scission is the primary mechanism in nylon degradation in the service environment. However, as is discussed more fully in the Appendix, changes in basic polymeric state are complex, and not necessarily unidirectional.

Change processes also include a variety of possible alterations of crystal state and of the intricate arrangement of ordered and disordered regions within the supra-molecular structure of the fiber. Some of these are "constructive" rather than destructive, but may lead to stiffening and embrittlement. The occasionally observed gain in apparent strength during early stages of some exposure studies is attributable to this further building of supra-molecular structure. The effect is not necessarily favorable, however, in terms of impact performance. It may also temporarily obscure simultaneous destructive processes, leading to a condition where rapid degradation may then occur.

Non-deteriorative changes at the fiber level may also lower the strength translation efficiency in the twisted and interlaced geometries of the final materials. This efficiency is also influenced by surface effects, fiber "set,"

7

and mechanical conditioning in the case of multiple-use parachutes. The general translation and realizable strength properties of the materials are also affected by localized changes which may be so minor in extent that their occurrence would be undetected in a bulk analysis of the material.

It is apparent that test data showing strength losses of the nylon materials are subject to much interpretation as to what has actually occurred. It is likely that in any given case a number of processes have been active, with the pattern determined by the original state of the specific material and the simultaneous and sequential combinations of influences. It should also be emphasized that retention of original specification test strength values is not to be taken as proof that "no changes" have occurred. Such an assumption may be very misleading and dangerous in predicting the effects of subsequent time and exposures.

These factors are covered in more detail in the Appendix, but are noted briefly here as background for consideration of the test data which follows.

III. Results of Specific Tests

The Army projects have been limited to laboratory evaluations of troop main parachutes with a range of jump histories, and of reserve parachutes having only storage and storage-plus-service (not deployed) histories. It was expected that other military service studies of emergency parachutes would yield further background information on the general effects of ageing and exposures encountered in inspections and repacks. However, the Army program did include a supplementary study of the relative influences of differing environments (excluding u-v exposure) by storing samples of component materials for 8 years in four climatic chambers.

A. Effects of Jump History on Troop Parachutes

The results of the several tests on T-10 troop parachutes with histories of up to 50 jumps have been reported previously[7]. Each jump-number group was a separate sampling, and the data thus reflect variables of original properties and environmental circumstances, in addition to the number of jumps and typically related time-in-service and maintenance histories.

8

However, the test values show a reasonable consistency with what now appears to be a rather common condition among parachute populations. Figure 3a illustrates the progression of average canopy fabric strengths and the range of values in the successive groups. A slight general trend is noted. More marked, however, is the increase in scatter starting with the 10-jump group. While a further widening of the range does not show until the 50-jump group, the predictability of the distribution in the total populations is appreciably lowered rather early in the jump history. Since increasing number of jumps did not show a pronounced continuing trend for the upper part of the ranges, it appears that the causes of the more distinct strength losses are largely coincidental rather than directly related to jump routines.

Figure 3b shows the progression of strength values of the suspension lines. What is probably a real but minor general trend of the order shown by the canopy fabrics is obscured by the rapid drop in test strength which is known to be due to mechanical effects of repeated loadings. This loss is progressive up to about 20 cycles, after which the cords apparently reach a stable configuration. The extent of this typical mechanical loss is roughly indicated by the upper values which level off at about 25 pounds below the specification requirement. The generally continuing drop in lower values is taken to reflect more basic degradation and possibly instances of overloaded lines in erratic parachute openings.

Since the thin canopy fabric is generally more vulnerable to actual deterioration by sunlight and other external influences, the more extreme losses of test strength of the cords are somewhat curious. Fluidity (See Appendix) values for both fabric and cords were in a very close range and probably little higher than original values, indicating that exposures had not been severe. It is surmised that the realizable strength of the braided cord structure is considerably more sensitive to minor and uneven changes in fiber characteristics than is the simple woven structure of the canopy fabric.

Impact strength data were available only on the 30, 40, and 50-jump group. The canopy fabric strength and elongation levels were in the range for new materials, and no trend was indicated. The cord impact strength values were also fairly normal except for a few distinctly low values in the 30-jump group. However, the elongations of the cords under impact were considerably below those found in new materials or which might normally be predicted from elongations at standard test speed.

9
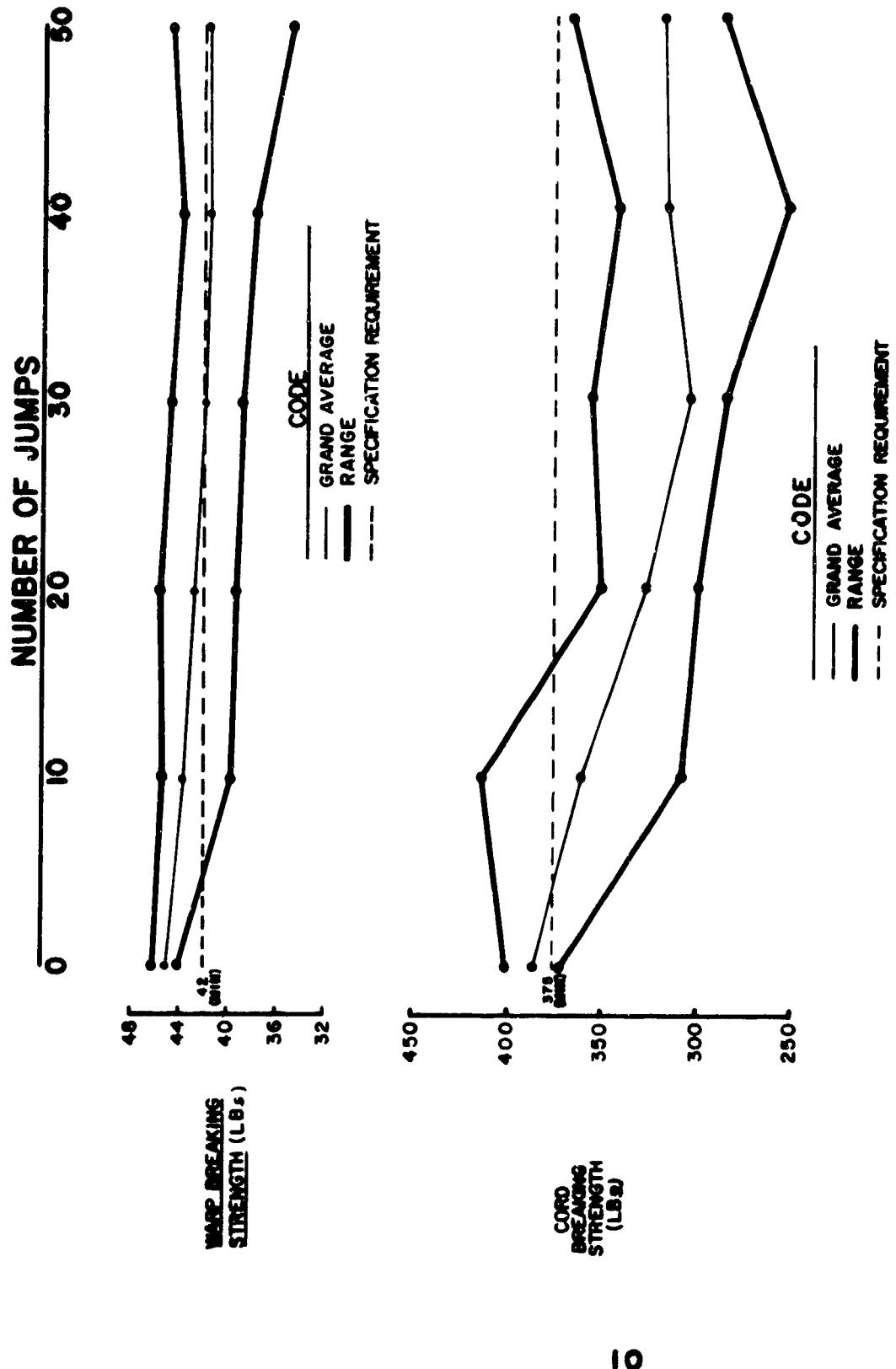
BREAKING STRENGTH of CANOPY FABRIC and SUSPENSION CORD from T-10 TROOP-TYPE PARACHUTES of 0 to 50 JUMPS

Fig. 3

The tests on Halo[8] and Sky-diver[9] parachutes which had been jumped 100 times gave results very comparable to those for the T-10 parachutes of up to 50 jumps. There was no clear indication that the higher number of jumps had caused progressive degradation. Canopy fabrics were still in quite good physical condition (though losses of air permeability were strongly indicated). Suspension lines showed lowered strength level at normal test speed and lowered elongation at impact, similar to those for lines from the T-10 series at 50 jumps.

With these results and the obvious fact that the sample parachutes had performed satisfactorily up to the designated number of jumps, it appears that repeated normal use up to the presently prescribed 100-jump limit does not directly produce a hazardous condition. However, the typical losses in suspension line strength and energy adsorption on impact make it apparent that the safety factors thought to be provided in the ratings based on specification tests requirements are not actually realized. The import is that the less typical parachutes which are degraded by unusual exposure or other causes will reach an unreliable performance level more quickly than would be predicted from the ratings.

Broader surveys to assess the incidence and extremity of the abnormal cases in a large parachute population at these high jump levels may not be warranted since most of these troop main parachutes are discarded for excessive mechanical damage and/or inspection criteria well before they reach the 100-jump limit. However, reservation should be made as to the general reliability of this limit because neither the operating nor the test programs reflect the possibility of parachutes approaching both the 10-year and the 100-jump limit simultaneously. A change in training programs or supply management could result in a build-up of old and much-used troop parachutes for which there are now no data. Reservations also have to be made as to the possibility of operations which would involve lengthier exposures before retrieval, or less skill in maintenance. Accordingly, though the 100-jump limit imposes no present economic penalty or apparent hazard, it should be made subject to review if there is any marked change in the governing circumstances. Meanwhile, it would be well to develop more stable suspension line constructions for future parachutes so that a greater safety factor will actually be realized.

11

The findings on multiple-use parachutes also raise the more general question as to the dominance of u-v exposure as a cause of degradation in any class of parachutes (excepting certain ejection seat lines.) With the duration of exposure at each jump, the total exposure is considerably greater than that encountered by reserve and emergency parachutes in typical service histories. If u-v is the major common factor, troop parachutes would show distinctly greater deterioration than stored or carried (but undeployed) equipment. No such general difference was found in the limited sampling and testing in these programs. However, this observation does not preclude that u-v exposure is a frequent cause of the small portion of more extreme cases.

B. Effects of Storage

The few tests on unissued Army parachutes start with that reported[10] in 1959 covering 13 Type 7-A reserve parachutes which were retired, without ever having been placed in service, under the then 7-year service life limit. Since the standard test values were well above specification minimums with one minor exception, it was concluded that any changes from the original strengths must have been minimal. Fluidity values were in the range for current new materials, from which it was concluded that no "chemical" degradation had occurred. Though the investigators limited their comments to the specific samples, and also made strong reservation that impact performance could not be predicted from slow speed tests, the findings were apparently taken as an indication that stored 7-year old reserve parachutes were not significantly changed from their original condition.

Whether or not the generalized conclusion was correct in fact, the test basis for it is to be questioned. The sampling was small and from only two manufacturers and a brief production period. Also, all sample units had most of their storage life in Japan where, as strongly indicated by the subsequent climatic chamber study, the generally humid atmosphere is one of the most favorable for retention of the physical properties. Accordingly, the samples represented a particular case rather than the range or the most typical portion of a 7-year old parachute population.

Ten of the sampled parachutes were again tested after 5 years additional storage in the New England climate[10]. Except for slight but probably significant losses in tear strength, the canopy fabric appeared to be generally unaffected. However, there were significant changes in suspension line strength in some of the test units, as shown in Table I. Whereas at 7 years the lines from

12

TABLE I

BREAKING STRENGTH OF SUSPENSION LINE CORDS FROM T-7A RESERVE PARACHUTES AFTER 7 AND 12 YEARS OF STORAGE

Parachute Ident.	Breaking Strength (lb)			Change
	7 Yrs Average	12 Yrs Average	12 Yrs Range	Average
25	590	604	580-615	+14
95	602	555	530-613	-47
366	578	601	585-610	+23
427	577	544	525-555	-33
12283	536	523	498-555	-13
12289	588	541	525-560	-47
12835	579	545	535-552	-34
13116	600	589	561-604	-11
13420	608	603	580-621	-5
13531	591	586	565-595	-5
Average	585	569		-16
High Five		597		
Low Five		542		
Specification minimum	550			

9 of the 10 units were still well above specification requirements, at 12 years the lines from 4 of the parachutes had dropped to below the requirement and another had dropped markedly from its 7-year value. The disparity shown by the various units is of particular significance, and illustrative of the complex nature of the degradation problem. Only one of the low average values at 12 years would have been predicted from the 7-year values. Among the individual lines, strengths ranged from 408 to 601 pounds. Since the 5-year additional storage conditions were identical for all samples, it must be concluded that real but not then apparent differences in internal state did exist at 7 years, and possibly all the way back to the original samples.

Since none of the line strengths were alarmingly below the specification minimum and the observed changes in fluidity were considered negligible, it was concluded that the noted losses at 12 years were due to some "physical" condition rather than true deterioration, and that the stored units were still serviceable. The impact tester was still not available, but one parachute was drop-tested with no material failure. The conclusion as to serviceable condition was probably valid, but in review it must be recognized that the limitations and arbitrariness of the original sampling still applied, and also that the additional 5-year storage was in only one and probably a rather favorable environment.

The more general conclusion from this test project on stored parachutes is that while prolonged time under reasonably favorable storage circumstances may have no apparent effect on some materials in the parachute population, it can have decided effects on others. The differences in susceptibility may not be distinguishable in earlier tests. What the range of disparity may be in any particular age class, or in the population as a whole, is not determinable by small-scale or intermediate evaluations.

C. Effects of Service Use Without Actual Deployment

A more recent test[11] of 10-year-old Type T-7 parachutes, which had been in service, though never deployed, included both white and camouflage types. This project also included high strain rate (impact) testing. The findings did not clearly evidence a hazardous condition, if the samples could be considered reasonably typical. However, the nature of the results illustrates some points of broad significance. Averaged data for these samples and the 12-year storage parachutes are summarized in Table 1.

TABLE II

PROPERTIES OF NYLON MATERIALS FROM T-7A PARACHUTES OF VARYING TYPES
AND HISTORIES

	From Service 10 yrs. old		Storage only 12 yrs. old	Spec.
	Camouflage	White	White	Req.
Fabric **Strength**				
Standard	60.9	56.4	60.7	50
Impact	67.8	60.8	69.8	(77)*
Elongation				
Standard	29.5	27.2	28.8	14
	24.9	21.2	24.6	(22)*
Line **Strength**				
Standard	528	574	569	550
Impact	349	344	367	(383)*
Elongation				
Standard	34.9	38.0	42.0	30
Impact	27.9	30.0	28.2	(29)*

Note: *Indicates typical values for current new materials. These
are not specification requirements, and may not correspond
to original properties of the older materials.

For the canopy fabric, the strength and elongation values
for the camouflage group from service and the white group from
storage were very close (also, the individual results were within
a small range), but those for the white group from service were
significantly lower, particularly so in the impact tests. Without
data on the original fabrics or service environments, no technical
interpretation of the observed differences can be made. However,
it is demonstrated that data from one subgroup cannot be used to
predict the condition of other subgroups or of the population as
a whole.

For the suspension lines, it is noted that those from the white parachutes from service had the highest average strength level at the standard rate of testing, and the lowest at impact. Whether this contrast reflects the original characteristics, the specific history, or both, the comparison shows that the relation of impact to static load performance can vary considerably between samples and groups.

The data for the suspension lines also illustrate one of the biggest problems with limited surveillance programs on old equipment. As was shown in Figure 1, representing distribution of strengths in the camouflage group, even in this small sampling the scatter of individual values ranged between plus 5% to minus 24% of the 550-pound specification minimum. The wide scatter is within as well as among units. For example, though three of the four values below 475 pounds were in parachutes having generally low values, one was in a parachute having both a high average and the highest individual value (578) among the 50 lines (10 per parachute) tested. Since original strengths generally exceed minimums by 5 to 15%, the actual losses were probably greater than indicated by comparison to specifications. Because of the designed safety factors, losses of this general magnitude might still perhaps be tolerated if it is known with certainty that this range is not greatly exceeded within the total population. The key problem is that as the group advances in age and service, the extreme cases are further removed from the norm, and the incidence of extreme cases increases. Accordingly, predictions as to the condition of the worst unit in the total population, or of the percentage of units falling below some defined lower limit of serviceability, became increasingly unreliable as the general trend proceeds.

An opportunity to gain a broader picture of distributions came about while developing a conversion procedure for overage U. S. Navy and Air Force emergency parachutes for cargo drop systems. This sampling(12) of 140 Type C-9 parachutes of 7, 8, and 9 years age from date of manufacture provided the most extensive surveillance of closely grouped age classes, and is also the most current to parachute populations now reaching the prescribed service limits.

The apparent trends in the norms and scatter are illustrated by the total distribution shown in Figure 2, separated by years of age as given in Figure 4 for canopy fabric, and for suspension lines in Figure 5. While the indicated trends could conceivably reflect only chance in the sampling, changes
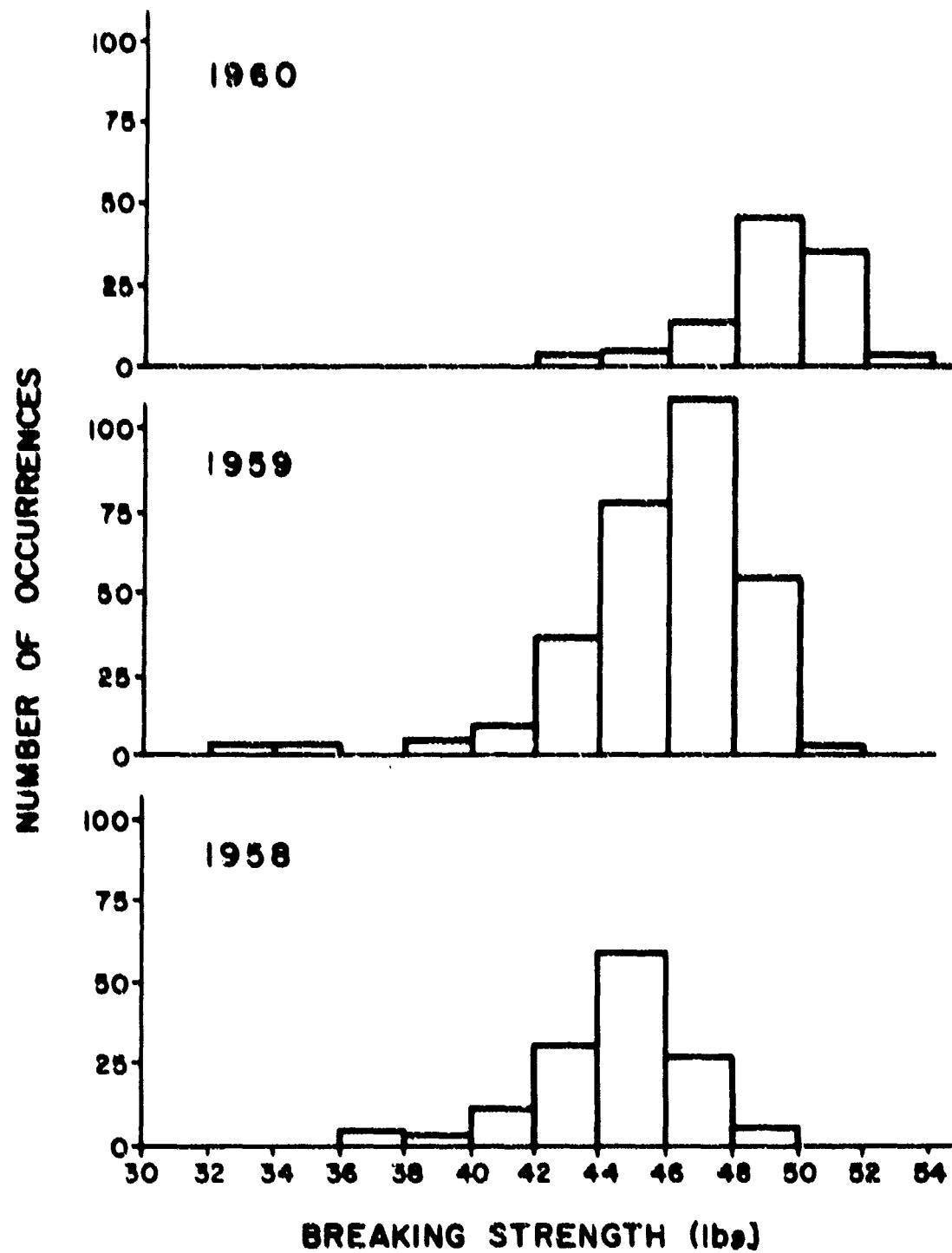
16

AGE CLASS DISTRIBUTION OF CLOTH BREAKING STRENGTH
RESULTS FROM 140 EMERGENCY PARACHUTES

FIG. 4

17
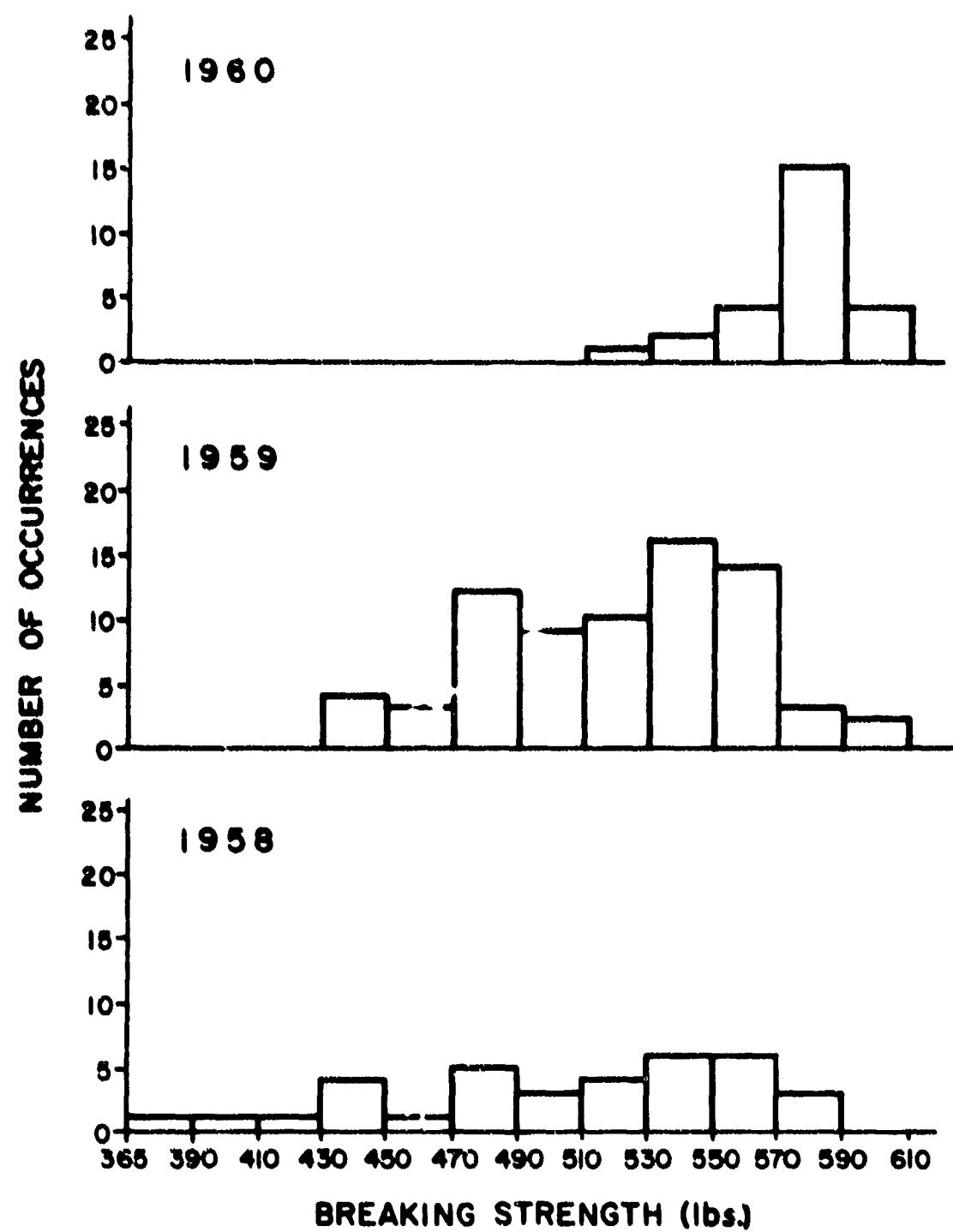
AGE CLASS DISTRIBUTION OF CORD BREAKING STRENGTH
RESULTS FROM 140 EMERGENCY PARACHUTES

FIG. 5

18

In the original materials during these successive years of production, or varying storage and service circumstances, they appear consistent with other evidences of what now appears to be the broad pattern as parachutes continue in age and service. This is characterized by a slow general progression of strength-reducing processes, but more particularly and seriously by a rather rapid increase of instances of units and component areas which have been affected very markedly.

U. S. Navy tests on emergency parachutes of differing ages and histories are summarized in a 1964 report[13]. Though the conclusion in that report as to the dominance of u-v exposure in causing parachute deterioration is not well supported by observations made herein, the data and other conclusions are believed to be generally consistent with the picture of the service life problem now proposed. The tabulation of laboratory test results from that report is reproduced here as Table III, and of fluidity values as Table IV.

It is noted that the correlation of strength loss with age is only roughly indicated by the findings, and that the progression of fluidity values with age is not apparent. It is believed that larger samplings per age class might have shown more semblance of the strength trend patterns indicated in Figures 4 and 5. However, if the apparent trend is more in the probability and accumulation of the less typical cases than it is of intrinsic time-dependent phenomena, the erratic pattern in age-strength relations in small samplings is to be expected. It is possible that at times this irregularity may exist in the total populations of successive age classes. For example, a particular 8-year class might contain more seriously degraded parachutes than the next older classes.

As to the causes of the "less typical" cases, a number of possibilities are known. Variations in material manufacture or processing may make a production lot unusually susceptible. Acidic breakdown products of residues or finishing compounds may deteriorate the material directly, or accelerate other degrading processes. Excessive heat, as for instance in storage close under a roof in a hot climate, may act directly or serve to promote other change mechanisms. Instances of prolonged exposure to sunlight or fluorescent lighting occur in maintenance operations. In addition to these uncommon circumstances, it is at least suspect that some instances of more marked strength loss reflect that materials undergoing slower change processes reach breakpoint conditions beyond which these or other processes proceed rather rapidly.

19

TABLE III

BREAKING STRENGTH OF MATERIALS FROM EMERGENCY PARACHUTES OF VARIOUS AGES AND HISTORIES

(Laboratory tests made after drop test, except as noted)

DATA FROM NARF TECH. REPORT No. 6-66 (13)

Age	No. of Prcht	Break (Lbs) (Raveled Strip) Warp Avg.	Range	Fill Avg.	Range	Suspension Line Break (Lbs) Avg.	Range
60 days[a]	9	45.8	45.5-46.5	44.1	44.0-44.2	519	488-535
5 yrs[a]	10	44.0	43.2-44.5	45.4	43.9-47.1	487	433-523
5 yrs	10	42.7	41.2-44.5	40.8	37.5-44.0	458	473-487
9 yrs	6	44.5	42.2-46.7	42.5	40.5-45.3	489	411-531
10 yrs	17	38.1	36.1-39.7	37.7	37.0-39.0	508	457-537
11 yrs[b]	16	43.3	39.7-47.5	42.1	39.0-46.0	501	464-535
11 yrs	9	39.7	34.4-45.5	38.2	32.5-43.6	503	418-574
12 yrs	3	44.2	43.1-44.8	42.3	38.7-44.2	497	448-530
15 yrs	18	37.8	30.8-41.8	37.0	28.8-41.0	494	398-543

a Storage only
b Not drop tested

20

TABLE IV

FLUIDITY VALUES OF MATERIALS FROM EMERGENCY PARACHUTES OF VARIOUS AGES

DATA FROM NARF TECH REPORT NO. 6-66[13]

Age (months)	Fluidity (Rhes)	
	Canopy	Suspension Line
2	1.2	-
19	1.2	1.2
41	1.6	1.5
60	1.5	-
65	1.4	1.4
118	3.2	-
120	1.8	-
123	2.9	1.6
128	1.5	1.5
130	1.9	1.5
131	2.0	1.8
135	1.8	1.8
135	1.8	1.7
140	1.7	1.5
140	1.9	1.6
144	2.0	1.0
180	1.9	1.8
181	1.8	1.4
181	1.6	1.8
181	1.6	1.8
182	1.8	1.6
182	1.8	1.7
182	1.6	1.5
182	1.6	1.5
183	1.6	1.6

21

D. Effects of Climatic Environment

From the climatic chamber study (14) it also appears that the climatic environment has considerable bearing on ageing effects of the nylon materials. In this program a variety of parachute materials were stored in the climatic chambers for 8 years and then re-tested following prolonged reconditioning in a standard atmosphere (70°F, 65% RH). The warm chambers simulated diurnal cycles of temperature and relative humidity (see bottom of Table VI), in climates characterized as Moderate Desert, Moist Tropical, and Temperate Summer. The cold chamber was maintained at 0°F. For the canopy fabrics, sets were draped openly, flat bundled and wrapped, and creased and wrapped. Since no significant changes were found in two years and the supply of samples was limited, intermediate testing was stopped. Testing was not resumed until the 9th year of storage.

It is not to be construed that elapsed time in these chambers is equivalent in its effects to that in the corresponding actual climates since the chamber conditions represent the peak range rather than the yearly average. However, unlike most laboratory evaluations, the acceleration is not by exceeding the realistic peak condition, and thus should not produce effects that do not occur, at some rate, during the real environmental exposure.

The findings for canopy fabrics are summarized in Table V, suspension lines in Table VI, and tapes in Table VII. The findings illustrate how specifically data in this field of investigation must be taken. The only generalities that can be drawn are that full exposure in hot dryness is unfavorable, and that a moist warm atmosphere is favorable to retention of strength properties. Beyond these quite well-supported observations, inconsistencies in the sample-climate-exposure relations upset any broad conclusions as to environmental influences on nylon materials as a class.

The individuality of the material samples is illustrated by several comparisons. For example, the 1.1-ounce OD fabrics from the moist tropical and the cold chambers showed almost identical slow speed strengths appreciably above the original values, but at high speed the strength of the fabric from the cold chamber was distinctly lower and probably was a true loss from the original. This contrast was also evidenced, though less distinctly, for the 1.1-ounce natural, cords, and tapes. However, for the 1.6-ounce twill, which also showed very similar slow speed strengths from these two chambers, the high speed strength was distinctly higher for the cold chamber sample.

22

TABLE V

BREAKING STRENGTH OF PARACHUTE CANOPY FABRICS
AFTER EIGHT YEARS STORAGE IN CLIMATIC CHAMBERS

Warp Breaking Strength (lb), 1" Ravel Strip

	1.1 oz Rip Stop (OD) Strain Rate (%/min)		1.1 oz Rip Stop (Natural) Strain Rate (%/min)		1.6 oz Twill (Natural) Strain Rate (%/min)	
	400	480,000	400	480,000	400	480,000
Specification Minimum	40		40		50	
Original Material	41.6(39-43)		42.0(41-44)		61.6(60-62)	
New Current Material	49	53	49	53	64	83
Moderate Desert						
Uncovered	39.6(32-45)	46.7(35-52)	31(27-35)	37.4(34-41)	30.4(42-45)	41.9(37-44)
Paper covered	45.5(44-47)	52.7(51-55)	46.1(40-50)	45.5(44-47)	55.7(52-60)	63.0(62-65)
Creased and covered	45.7(45-47)	52.2(51-53)	41.4(38-45)	52.3(51-55)	53.6(47-60)	59.8(56-63)
Temperate Summer						
Uncovered	40.6(23-45)	46.7(40-50)	31.1(10-41)	31.8(18-45)	50.6(32-59)	52.9(35-72)
Paper covered	45.2(45-47)	49.6(46-55)	45.5(44-51)	51.3(47-55)	60.5(59-63)	63.4(58-65)
Creased and covered	45.4(45-46)	53.5(53-55)	41.3(39-45)	48.7(44-54)	57.2'57-60)	62.9(56-67)
Moist Tropical						
Uncovered	44.6(43-47)	52.2(50-55)	41.3(31-44)	49.6(44-52)	60.8(60-62)	71.5(66-74)
Paper covered	47.8(46-51)	57.3(50-55)	45.8(41-50)	53.8(51-56)	60.8(58-63)	62.9(55-67)
Creased and covered	47.3(44-51)	54.1(52-56)	43.9(38-49)	52.2(47-56)	58.4(50-62)	63.1(56-66)
Cold						
Uncovered	43.5(42-45)	42.8(37-50)	43.2(42-45)	46.7(43-50)	61.7(60-64)	70.0(67-77)
Paper covered	48.7(45-52)	42.8(35-47)	49.2(48-52)	48.3(47-50)	60.1(58-62)	69.4(68-70)
Creased and covered	46.1(46-47)	41.1(33-47)	45.0(44-46)	48.9(45-52)	62.5(62-64)	69.4(68-70)

23

TABLE VI

BREAKING STRENGTH AND ELONGATION OF PARACHUTE SUSPENSION LINE CORD
AFTER EIGHT YEARS STORAGE IN CLIMATIC CHAMBERS

Breaking Strength (lb)

	Type III Cord (OD) Strain Rate (%/min)		Type III Cord (Natural) Strain Rate (%/min)	
	21	45,000	21	45,000
Specification Minimum				
Original Material	550		550	
New Current Material	574(567-583)	383	590(572-601)	383
	621		621	
Moderate Desert	519(507-548)	361(342-380)	509(458-552)	342
Temperate Summer	554(540-568)	389(370-399)	586(567-601)	356(351-361)
Moist Tropical	581(557-590)	386(380-389)	581(577-585)	383(380-418)
Cold	571(563-578)	364(351-370)	595(591-598)	390(361-418)

Elongation (%)

	Type III Cord (OD)		Type III Cord (Natural)	
	21	45,000	21	45,000
Specification Minimum				
New Current Material	30	29	30	29
	41		41	
Moderate Desert	36.5	25.7	34.6	28.6
Temperate Summer	39.6	27.2	38.6	23.2
Moist Tropical	42.4	27.6	40.2	27.4
Cold	39.4	27.3	43.3	25.4

Moderate Desert - 80-130°F, 12-51% R.H.
Temperate Summer - 78-106°F, 30-64% R.H.
Moist Tropical - 74-103°F, 50-96% R.H.
Cold - 0°F

TABLE VII

BREAKING STRENGTH AND ELONGATION AT LOW AND HIGH STRAIN RATES OF NYLON
REINFORCING TAPE STORED IN PAPER WRAPPERS IN FOUR CLIMATIC CHAMBERS

Breaking Strength (lb)

	½" Tape (OD) Strain Rate (%/min)		¼" Tape (Natural) Strain Rate (%/min)	
	21	45,000	21	45,000
Specification Minimum	500		500	
Original Material	574(567-583)		590(572-601)	
Moderate Desert	534(522-550)	380	443(428-468)	310
Temperate Summer	561(545-569)	374	535(523-548)	377
Moist Tropical	566(564-568)	383	545(533-553)	399
Cold	562(545-582)	351	-	-
Original	569		566	

Elongation (%)

	21	45,000	21	45,000
Moderate Desert	37.3	25.9	27.3	18.7
Temperate Summer	39.3	26.4	29.6	21.5
Moist Tropical	40.9	28.0	33.2	24.6
Cold	40.7	26.7	-	-

Another example is that while the 1.1-ounce (both OD and natural) fabric from the moist tropical and cold chambers showed an increase of slow speed strengths over the originals, this increase was not evidenced in the 1.6-ounce twill, cords, or tape.

That the specificity is not necessarily related to material construction (rip-stop, twill, cord, etc.) is shown by comparing the OD and natural 1.1-ounce fabric in terms of toughness index. (The index reflects energy to break, which is more closely indicative of performance capability in these applications than is rupture strength.) The least complicated case of the flat wrapped samples is taken for illustration (Table VIII).

TABLE VIII

WARP TOUGHNESS INDEX AT SLOW AND IMPACT STRAIN RATES OF
1.1 OUNCE RIP-STOP FABRICS FROM CLIMATIC STORAGE (in. lb/in.)

	OD		Natural	
	Slow	Impact	Slow	Impact
Moderate Desert	7.7	6.9	6.1	4.8
Temperate Summer	7.6	6.5	6.6	6.4
Moist Tropical	8.5	7.0	6.8	6.9
Cold	8.1	4.1	8.0	5.0
Original	7.1	*	6.3	*

*For new rip-stop fabric the toughness indices at slow and impact speeds are usually in the same range.

For the first two climatic conditions, the slow speed values for both materials were roughly similar to the originals, but for the third condition, the OD fabric value was exceptionally high. On impact, the two fabrics had close agreement for both the temperate summer and moist tropical storage, but the natural fabric from both the moderate desert and cold conditions was exceptionally low in toughness. In contrast, for the OD fabric, only the value for the cold chamber sample was distinctly low.

In the strength comparison of OD and natural tapes, the natural sample from the moderate desert chamber was very much the lower at both slow and impact test speeds. For the suspension cords, the OD and natural samples from the moderate desert chamber were equally low, and at both test speeds. In other comparisons,

26

not detailed here, some sample-climate combinations showed losses
of both rupture strength and elongation, suggesting changes which
led to embrittlement. Others were low primarily in elongation,
suggesting a general stiffening of the material; and a few others
gave some indication of actual toughening.

Fluidity values obtained from the climatic storage
samples also showed the diversity of changes between samples and
environments, as in Table IX.

TABLE IX

STRENGTH AND FLUIDITY VALUES OF 1.1-OUNCE RIP-STOP FABRIC
AFTER 8-YEAR STORAGE IN CLIMATIC CHAMBERS

	Strength (lbs)	Fluidity
Original	42	1.2
		(assumed as typical of new material)
Moderate Desert		
Natural	25-37	1.85 - 2.08
OD	32-40	1.28
Temperate Summer		
Natural	13-20	1.87 - 2.10
OD	29-43	1.60 - 1.48
Moist Tropical		
Natural	35-37	1.48 - 1.59
OD	45-47	1.56

Under the moderate desert condition both samples had lost
strength appreciably, but the fluidity of the OD sample had been
scarcely changed. The natural fabric had lost considerably more
strength in the temperate summer than in the moderate desert
condition, but the fluidity values were the same. The OD samples
lost more strength in the temperate summer than in the moist
tropical condition, but the fluidities were in the same range.
These comparisons cannot be taken precisely because of the
variability between local areas of the samples, but the poor
correlation of strength and fluidity values is characteristic of
data from studies involving a variety of materials and/or histories.
It is fully evident that serious strength losses can occur under
certain circumstances without the occurrence of general polymeric
breakdown. It is also indicated that some degree of polymeric

27

degradation can occur without apparent effect on mechanical properties. These observations suggest that the semblance of correlation appearing in some test series may be coincidental rather than being reflections of a single change phenomenon.

The climatic chamber study raises many questions as to actual change mechanisms, but the major import of the findings can be stated as:

1. Among the several nylon parachute materials, there were marked differences in the changes of mechanical properties which occurred with prolonged time in each of the climatic conditions.

2. The nature and degree of the effects among the sample-climate combinations were very diverse, and presumably reflect a considerable variety of internal change patterns.

3. The effects were frequently very local within samples and between adjacent samples, and variability increased markedly with degree of average strength loss.

4. The losses in strength properties occurred without u-v exposure and under conditions which (though untypical in the sense that each specimen had only one sustained climatic exposure) were not unrealistic in terms of temperatures and relative humidities that might be encountered in service.

The results of the climatic storage study are believed to be consistent with the findings of the tests on aged parachutes from real storage and service conditions. Together, they support the view of the major service life problem as that of the diversity and unpredictability of effects on the parachute materials rather than that of a pervasive and consistent trend.

E. Summary

Analysis of findings from test projects and supporting studies provide the following conclusions regarding service life limits and the nature of the nylon parachute degradation problem:

1. The presently prescribed service limits and repair cost limit schedules for U. S. Army personnel parachutes should not be extended.

2. The premise of consistent and pervasive strength loss trends, which, if valid, would allow reasonably precise determination of generally appropriate service life limits, is not substantiated.

3. The effects of age alone, number of jumps, time in storage, time in service, and ultraviolet exposure in normal service routines, are not distinctive and predictable. (Exception is the initial loss in suspension line strength in repeated jumps, attributed to structural changes.)

4. The risk potential within older parachute populations is in the wide distribution and marked exceptions, rather than in the average or predominating trend.

5. There are considerable differences in susceptibility among material types and lots, and a number of degradation influences, mechanisms, and resulting effects.

6. The validity of small samplings decreases markedly as parachute populations increase in age and service.

7. The effects of subsequent ageing and external influences cannot be predicted from conventional test data on new or partially aged materials.

8. The system of reliability control by standard service life limits cannot satisfy, simultaneously, the requirements for safety and the economical realization of potential unit-years of service.

9. Improvements in reliability assurance and total economy would be realized only through extensive routine surveillance, product improvement and control, protective systems, and means for on-site evaluations of parachutes individually.

IV. Present Status and Progress

A. Light and Heat-Resistant Nylon

All of the service life data so far obtained have been based on materials produced prior to the introduction of "light and heat resistant" nylon in 1963. Use of the more resistant nylon yarn is expected to significantly reduce the rate of deterioration of those parachutes which are exposed to considerable sunlight and extreme heat. However, the change to the resistant yarns in all component materials is not yet fully completed, and it has been found that the resistance of the final materials has varied greatly due to differences in dyeing and finishing processes. It will be 1968 before all of the materials being procured will be consistently at the higher levels of u-v and heat resistance now

possible to obtain with these yarns. Accordingly, though it can be expected that a higher proportion of parachutes of the 1963 through 1967 production year classes will be in better condition when 7-10 years old than in prior classes at that age, the range of conditions and the degree of strength loss in the extreme cases might not be significantly different.

The fully realizable benefits from the use of the light and heat-resistant nylon are yet unknown. There are practically no data on a true time basis to indicate whether the newer materials have greater general stability or specific resistance to other likely causes of degradation. It must currently be assumed that change phenomena at the supra-molecular and final structure level will not be much different from those in the older materials. Also, it should probably be assumed that the resistance properties may diminish with time under some environmental or use circumstances.

B. Process Improvements

Under a separate applications engineering task the U. S. Army Natick Laboratories is developing and consolidating the technology of materials processing and dyeing to assure maximum light and heat resistance now practical in forthcoming procurements. The improvements should increase the average service life potential and uniformity of conditions within the new equipment classes as they approach maturity.

C. Surveillance

Test projects under the instant task have been terminated.

D. Research

A study of the effects of dehydration and possible restorative treatments, as suggested by the findings of the climatic storage study, is underway at the U. S. Army Natick Laboratories.

E. Future Programs

The findings and conclusions from this task and related U. S. Navy and Air Force studies are the basis for proposals prepared jointly by the materials technologists of the three military services and submitted to the Joint Technical Coordinating Group for Aerial Delivery, through and with the endorsement of Subgroup B - Parachutes, at meeting 7-8 November 1967.

V. References

(U. S. Army Natick Laboratories report series, except as noted)

1. Weiner, L. I., Some Aspects of the Evaluation of the Useful Life of Nylon Parachutes and Parachute Materials, Textile Eng. Lab. Report No. 155, August 1956.

2. Yolland, W. E. C., Safe Life Span of Parachutes in Service and Storage, Textile Eng. Lab. Report No. 190, June 1956.

3. Dogliotti, E. C., et al, Stability of Nylon Parachute Materials During Storage, Mat. Res. & Eng. Report No. 64-4, March 1964.

4. Boone, J. D., Actual Extent of Useful Life of Parachute Canopy, U. S. Naval Parachute Facility, Tech. Report 2-61, April 1961.

5. as 4., Part II, Tech. Report 2-63, June 1963.

6. McGrath, J. C., Ageing Characteristics of Polyamide Fibrous Materials Used in Personnel Decelerators, Wright Air Development Division, WADD Tech. Note 61-2, February 1961.

7. Figucia, F., Jr., Effect of Service History on Nylon Components of T-10 Troop-Type Personnel Parachutes with Histories of 0-50 Jumps, C&OML, Mat. Exam. Report No. 8338, March 1967.

8. Figucia, F., Jr., Laboratory Evaluation of Halo Parachutes After 100 Jumps, C&OML Mat. Exam. Report No. 8348, July 1967.

9. Figucia, F., Jr., Laboratory Evaluation of Sky Diver Parachutes After 100 Jumps, C&OML, Mat. Exam. Report No. 8349, August 1967.

10. Litt, J. T., et al, Evaluation of Textile Components of Overage T-7A Reserve Parachutes, Textile Eng. Lab. Report No. 245, May 1959.

11. Figucia, F., Jr., Laboratory Evaluation of Aged Reserve Parachutes, C&OML, Mat. Exam. Report No. 8342, June 1967.

V. <u>References</u> (cont'd)

12. Figucia, F., Jr., "Analysis of Age-Strength Relationships in Emergency Parachutes Recalled from Service, C&OML, Mat. Exam. Report No. 8358, September 1967.

13. Boone, J. D., "Actual Extent of Useful Life of Parachute Canopy, Part III, Navy Aerospace Recovery Facility, Tech. Report No. 6-66, December 1966.

14. Figucia, F., Jr., and Wells, R. D., Physical Properties of Nylon Parachute Materials After 8 Years Storage in Climatic Chambers, C&OML, Mat. Exam. Report No. 8346, June 1967.

APPENDIX

MECHANISMS OF DEGRADATION IN NYLON FIBERS [*]

As suggested in the main text of the report, three levels of structure contribute to and govern the mechanical properties of the final materials. Changes may occur independently at each level, but are more likely to occur in various simultaneous and sequential combinations according to the state of the material and the patterns of causative influences. Some changes which are not truly deteriorative may adversely affect the translation of intrinsic properties and the resulting mechanical characteristics.

Though a number of degradation phenomena have been noted by various investigators, there has been a common tendency to consider the strength losses observed under common circumstances primarily as the result of chemical breakdown of the polymeric chain system. Evidences of these depolymerizing processes are frequently found in degraded materials, as in solution viscosity (fluidity) changes and end-group determinations. However, these solely chemical concepts are incomplete in explanation of a number of practical observations. Also, the relationships of the polymeric states and the physical properties are not well defined.

The major portion of the nylon polymer is of linear hydrocarbon segments which are themselves stable under normal environments. However, these segments are connected by amide groups which are affected by various chemical agents and energy processes. The amide groups are doubly important to the physical properties of the polymer since in addition to the linear linkage they are sites for intermolecular hydrogen bonding. It is this lateral bonding which integrates the otherwise flexible and mobile chains into a system of high crystallinity and cohesive energy density.

Chemical degradation is usually the result of the interaction of a number of causative and governing factors as:

Ultraviolet radiation	Humidity
Heat	Intensity
Oxygen	Time
Acids	Low molecular weight constituents
Specific organic compounds	

33

While some information can be gained by model studies involving these factors independently, the change mechanisms and their effects are not necessarily the same as will occur under the various combinations of actual exposures in service.

Breakdown initiated at one amide group may or may not proceed along the same chain, and the progression of scission patterns is difficult to trace. Analysis of the course of the polymeric breakdown in degraded materials from service has been largely limited to gross indications of changes of the molecular length characteristics, and most commonly by viscometry. In studies of degradation by u-v exposure and by strong mineral acids[1] good correlation of viscosity with strength properties has been found. However, the method is not as sensitive to initial changes in nylon as it is for other materials such as cellulosic fibers, and correlations are rather poor when more than one causative factor is involved. An inherent difficulty is that like most other analytical systems such as end-group determinations[2, 3], viscometry reflects the average or bulk condition whereas the chain scission may be localized at critical sites. Also, solution viscosity gives no indication of the state of secondary bonding between the primary chains. In consequence, while viscosity changes do indicate that significant chemical degradation has occurred, they are only a rough measure of the general state of the material. Methods which give more information on chain length distributions may prove useful in future studies.

Ultraviolet radiation of nylon has received considerable attention and is one of the best defined degradative influences on the polymer[4, 5]. Actinic radiation of nylon results in primarily a surface reaction as evidenced by darkening and gumminess in the case of extreme radiation. However, with the extremely high surface to volume ratio in textile fibers, effects of the incident radiation can lead from mild alteration in physical properties to the total destruction of the material.

Two mechanisms for molecular breakdown reactions have been postulated as caused by ultraviolet radiation of nylon. The first is a photolysis into both free radicals and smaller molecules which is initiated by shorter wave lengths of light (below 3000 Å) in the absence of oxygen. The products of photolysis are carbon monoxide, water, saturated and unsaturated hydrocarbons, carboxylic acids, N-alkylamides and primary amines both of different chain lengths than those in the polymer. The second mechanism of breakdown may be considered as a photo-oxidation brought about by the action of longer wave lengths of

34

light (greater than 3000 $\overset{o}{A}$) in the presence of atmospheric oxygen, leading to the additional products of carbon dioxide and aldehydes. The oxidative attack occurs predominantly at the methylene alpha to the nitrogen of the amide, resulting in peroxidation with subsequent breakdown of the alkoxy radical formed.

Mechanisms can be written for both the photolysis and photo-oxidation reactions which explain the formation of the products by free radical initiation, propagation, and termination. These mechanisms represent the predominant mode of molecular breakdown. However, the process which occurs is exceedingly complex and it should be recognized that other associated mechanisms are functioning at the same time. The photolysis reaction leads to both chain scission and cross-linking. The cross-linking is probably due to the formation of unsaturated hydrocarbons which, during the course of the free radical reaction, are able to react with radicals in the polymer chain and produce the cross-links. In an actual environmental exposure, both photolysis and photo-oxidation occur simultaneously, which leads to the relatively small amount of cross-linking observed and the predominance of chain scission[6-8]. In the case of delustered nylon which contains titanium dioxide, the reaction products are found to be the same as those for bright nylon. The rate of degradation of properties in delustered nylon is much greater than for the bright nylon although relatively more chemical change has been found for the latter when both are exposed equally. The explanation may be in the photo ensitizing action of the titanium dioxide bringing about more loc. lized degradation around the delustering particles, resulting in larger interruptions of the system and greater loss of mechanical properties.

The photolytic processes during radiation are diffusion-controlled. Two types of diffusion can be considered in the polymer system. One is gaseous diffusion which is relatively rapid and the other is diffusion of polymer chain segments which is quite slow. Due to the slow diffusion rate of the polymer chain segments, a dark reaction has been observed by the appearance of an absorption band at 2900 $\overset{o}{A}$. The intensity of this band increases on storage in the dark after irradiation, and has been postulated as being identified with a peroxy-free radical at the end of a chain segment. Its reaction rate is diffusion-controlled by the mobility of the chain segment in the polymer matrix[9]. This provides evidence for a continuing reaction in stored nylon after initial ultraviolet exposure.

35

Considerable effort has been expended in developing protective measures to allow service of nylon textile components in applications which involve exposure. These protective measures vary from incasement of the nylon component with a covering which degrades but is not required to sustain tensile stress, to actual incorporation of inhibitor in the polymer. Carbon black has been long known as an effective stabilizer against radiation but the color is not acceptable in most applications. A great number of stabilizers have been put to use in improving the light and heat resistance of nylon but much of this information is proprietary. Various stabilizers which have been noted in the literature include mercaptobenzothiazole, syringic acid, various phenolics, and inorganic salts of chromium, copper, and manganese.

The susceptibility of nylon to u-v degradation is also much influenced by the dyes used for coloration. Since it had been frequently observed that dyed samples had degraded less than undyed ones in exposure comparisons, there was a tendency to think of the dye substance acting as a significant barrier to penetration. However, dyestuffs differ widely in their effects, and some act to accelerate degradation. Apparently, the phenomena involved are rather complex and may include interactions between the nylon and the dye, and various patterns of the breakdown process, as well as the reaction of the dyestuff itself to the u-v radiation.

Comparatively little information is available on the action of normally encountered amounts of thermal energy on nylon. Reports which have been published[10.12] are mostly on the effects of elevated temperatures which lead to pyrolysis of the polymer. The products of pyrolysis are carbon dioxide, cyclic ketones, diamines, primary amines, hydrocarbons, ammonia, and water. Nylon exposed in the presence of oxygen at temperatures of 100°C to 140°C has shown losses in tensile strength to be due primarily to oxidation[13]. A mechanism similar to the free radical breakdown of nylon exposed to ultraviolet light could be proposed, involving a peroxy radical at the carbon alpha to nitrogen in the amide group, and also breakage at the methylene-carbonyl bond, with both processes leading to depolymerization. Upon heating, considerable physical changes take place in the polymer morphology leading, at times, to initial increases in strength which may be due to shrinkage of the drawn fiber caused by chain segment relaxation. Slight increases in strength on heating are more than offset as heating continues and oxidative processes as well as other physical changes predominate.

36

Little information is available on the effects of oxygen on
nylon without the initiating effects of heat or ultraviolet
radiation. Slow oxidation of nylon would be expected during long
storage. However, the changes that could be observed may be
insignificantly small compared with other aging effects such as
alteration of the crystalline structure, loss of plasticizing
low molecular weight compounds, etc.

The action of various chemical compounds on nylon usually
results in swelling, solubilization, and hydrolysis. Nylon textile
components in service may encounter a variety of chemical compounds
and it is difficult, at times, to determine after the fact which
types of compounds have acted on the nylon. Air pollution in and
around large cities and industrial plants increases each year and
adds to the chance and extent of possible exposure of nylon
materials to detrimental influences. The products which
contribute to air pollution are various, but ozone and sulfur
dioxide are common. While ozone alone does not affect nylon
appreciably, with the combined effects of heat and light it can
cause considerable damage. Sulfur dioxide can react with moisture
present in nylon and produce sulfurous acid, causing degradation.
Effluent gasses from industrial plants may contain harmful
chemicals, especially phenolic or acidic compounds and a number
are noted which act as solvents for nylon. These are not
ordinarily considered in the normal service life of a textile
component. However, with the wide variety of atmospheric
components and possible exposure to plasticizing material from
other neighboring materials, these compounds may exert an
unsuspected influence on nylon.

Nylon is readily soluble in phenol, n-cresol, xylenols and
formic acid, as well as strong mineral acids. It is slightly
soluble in crotyl phenol, sec-amylphenol, o-allylphenol,
glycerol mono and dichloro hydrins, ethylene bromo and chloro-
hydrin, acetic acid, lactic acid, thioglycolic acid, 2, 3
dibromo propane and phenyl ethyl alcohol. All of these solvents
act on nylon by breaking the hydrogen bonds between molecules,
leading to swelling of the polymer and finally ending with
complete separation of the molecules. The polymer molecules
have then formed stable hydrogen bonds with the solvent molecules.
Polyamides may also be hydrolized, but relatively severe
conditions are required. Other reactions of polyamides which
have been reported are amine-amide and amide-amide interchange
reactions[14]. These reactions are similar to the familiar ester
interchange reactions. However, their significance here is
probably low, since the material would have changed considerably
by other processes before an activating temperature could be
reached.

37

In the overall situation, polymeric degradation within nylon parachute materials in service is most likely to occur from u-v exposure, and in some cases by heat-induced oxidation. However, with the proliferation and build-up of possible contaminants from industrial wastes, agricultural chemicals, plasticized organic materials, etc., instances of degradation from those causes may be more common in the future.

The arrangement of the polymeric chains within the fiber structure develop and control the mechanical response properties which make the materials useful. Due to random elements in the polymer growth processes themselves, and to both internal and external variables in processes of fiber formation and subsequent treatments, the arrangements represent a wide range of patterns and distributions which can be only generally characterized. Earlier models for characterization were within the concept that the structure could be considered a two-phase system with distinct crystalline and amorphous regions. This model served rather successfully in relating qualitatively and sometimes quantitatively a number of bulk properties such as density, swelling, and melting behavior. However, it was not adequate in other respects, and did not encompass features of polymer organization subsequently revealed at the optical and electron microscope level[15-18].

The now most widely accepted model of the unoriented bulk polymer structure is one primarily of lamellar platelet-like crystals similar to those developed in crystallization from dilute solution. In these platelets the polymer chains are folded back and forth in pleated fashion with the chain direction essentially perpendicular to the base. The connectivity which gives structural and mechanical integrity is provided by amorphous chain segments which emerge and traverse from one platelet to another in rather random fashion[19]. The platelet growth is accompanied by crystal branching which serves to fill the space in more spherulitic or radial patterns. The branch structure is more particularly of the less crystallizable portions which in nylon are the lower molecular weight chains. Further crystallization of the intralamellar material may continue for a long period of time after the main crystallization front passes. Since this phase is not fully integrated[20] into the bulk structure, it does not directly contribute in a major way to the support of an imposed stress. However, it does act to plasticize the system and enhance resilience.

38

The structure of drawn polymers, as in high tenacity fibers, is still controversial, but it is believed that in cold drawing the elements or groups of the original lamellar platelets[21, 22] are separated from the disrupted spherulites by the drawing process, and become oriented with the molecular chain axis in the stretch direction. In nylon it does not appear that drawing increases the percentage crystallinity, but there is evidence that in heat-setting or annealing, further refolding into the platelet-type structure occurs[23]. With any commercially produced fiber the structure resulting from the thermo-mechanical history would be a composite of these elements of order.

In terms of these models certain qualitative and rather speculative conclusions can be drawn regarding the effects of chemical or structural alterations on the fiber mechanical properties. It is evident that the stress will not be uniformly distributed over all molecular chains, but will be borne mainly by the tie chains in the less ordered and less dense regions. Moreover, the distribution of stress among these amorphous chain segments will not be homogeneous, but will depend on orientation and attendant local structural details. Though both the crystalline and amorphous regions participate in reversible extension of the fiber, the rupture of chains would occur almost exclusively in the intercrystalline zones. Rupture of the polymer is usually considered as a cascade process[24] initiated by breaking of those chains subjected to disproportionate stress. Rupture patterns in the fibers will also be sensitive to grosser discontinuities and morphological features[25].

The sorption and diffusion of oxygen and other foreign gaseous and liquid materials will be restricted to the amorphous regions[26] and, therefore, the chemically mediated chain scission processes will also be localized in these regions which have the major stress-bearing role. It might well occur that the mechanical behavior of the fiber would be markedly affected by alterations of the key link elements which are so minor in proportion to the whole that they would be difficult to detect by chemical means. Moreover, scission will occur with higher frequency in the larger molecules because they have the most bonds and because they have the greater probability of contributing the interlamellar tie chains which form the more accessible regions. Accordingly, a weight-average molecular weight method of determination would be the most sensitive to changes by these scission patterns. For inherent accuracy, dilute solution viscosity, which also weights the higher molecular weight species, is the method of choice.

Changes in the mechanical behavior of the fiber may also be
due to changes in the physical or supra-molecular structure. The
newly formed material represents a metastable state in which both
mechanical and thermodynamic stresses provide a driving force for
continued structural changes. The usually observed slow increase
in modulus with time is attributed to the continued crystallization
of residual amorphous chains and to the perfection of crystalline
regions. This process of consolidation will affect the stress
response and translation of the fiber strength into the final
material, and can lead to increased embrittlement of the fiber
itself. The presence of local modes of chain motion[27, 28]
which occur in both the crystalline and amorphous regions might
lead to other structural changes over the long term. In nylon,
these stress-relieving processes would be facilitated by the
plasticization effect of sorbed water in the system which is
either bound through hydrogen-bonding to the amide groups or is
present as clusters around favorable electrostatic sites when
present in amounts greater than two percent[29]. Two forms of
elasticity account for polymeric behavior. These are
instantaneous elasticity due to bond deformation and delayed
elasticity which represents chain segment motion. This last
delayed elasticity is importantly affected in the deformation of
moist nylon. Delayed elasticity takes place in the amorphous
regions at temperatures above the glass transition temperature,
resulting in alignment of chain segments with corresponding
orientation of crystalline lamellae in the direction of stress.
The deformation mechanisms for moist and dry nylon have been
found to be different. The different mechanisms are due to the
plasticizing action of sorbed moisture. Sorbed moisture lowers
the glass transition temperature and permits conformational
changes in the amorphous segments which lead to a rubber-like
elastic deformation and increased resistance to an impact
stress[16].

Under favorable conditions these changes may actually increase
the tenacity and ultimate elongation of the fiber, and under other
conditions serve to offset the apparent effects of simultaneous
adverse changes. In consequence, a material may, for a considerable
period of time, show no change in normal mechanical characteriza-
tions and yet be undergoing internal processes which might
predispose it (or possibly even enhance the resistance of the
material) to change by subsequent influences. In this connection,
it is interesting to note that in studies[13, 30] of the "heat
setting" of nylon it was found that the process was accompanied by
changes in long-period spacing and crystallinity, but not by
changes in crystal orientation and molecular weight. This indicates

40

that only very special rather than general aspects of structure
have been affected by the treatment, and that these local changes
are markedly influential in the alteration of over-all mechanical
properties. This sensitivity to local changes would presumably
hold for adverse as well as favorable processes.

It is evident that the microscopically heterogeneous nature of
the crystalline polymer fibers is such that minor amounts of
chemical and physical changes can exert large effects on
properties. This, together with the interplay of uncontrollable
molecular structure factors, can lead to a wide variation in the
long-term response of "apparently" similar samples to similar
environments, and of identical samples to somewhat different
environments. The complexity of the possibilities presents many
difficulties in determination of the actual events responsible
for changes in mechanical properties, and means a low level of
predictability from data reflecting only gross properties and
bulk composition.

Nearly all of the data on the effects of degradation from
both service materials and samples used in controlled studies are
in terms of strength test results on the complete material. These
data are at best only one characterization of physical condition,
and they reflect a complicated translation of the fiber properties
in the configuration of the yarn and fabric or cord assembly.
Observed strength losses may in some cases be due to an increase
in modulus or other changes of fiber response characteristics
which adversely affect the translation, though the fibers
themselves have not lost (and may have gained) tenacity. On the
other hand, the sometimes noted gain in material strength under
certain conditions may be due to stress relaxation within the
assembly, which improves translation, without any change in
fiber tenacity having occurred. In some instances changes are
evidenced by impact but not by slow-speed testing, and other
instances have been noted where the effect has been more apparent
at slow speed. While these comparisons may partly reflect
similar response properties of the fibers, it is probable that
translation effects are also involved.

With all the possibilities for changes within the fibers and
in their translation efficiency, it is obvious that conventional
test values on aged and exposed nylon materials are not as
validly predictive of practical performance as they may have been
for the material when new. Also, strength test data are not very
informative as to what has actually occurred within the material,
nor of what may occur in subsequent exposures and time. More
explicit characterization methods will be required to close the
gap between the practical and the research approaches to the
nylon degradation problem..

41.

REFERENCES AND SUPPLEMENTAL BIBLIOGRAPHY

1. Boulton, J. and Jackson, D.L.C., The Fluidity of Nylon Solutions in m Cresol: Measurement of Chemical Damage in Nylon Textiles, Journal Soc. Dyers and Colourists 59, 25 (1943).

2. Taylor, G.B., The Relation of the Viscosity of Nylon Solutions in Formic Acid to Molecular Weight as Determined by End-Group Measurements, Journal Am. Chem. Soc. 69, 635 (1947).

3. Elias, V.H. and Schumacher, R., Über das Lösungsverhalten von Nylon 66, Makromal Chem. 76, 23 (1964).

4. Appleby, D.K., The Action of Light on Textiles, Amer. Dyestuff Reporter 38, 149 (1949).

5. Searle, N.Z. and Hirt, R.C., Bibliography on Ultraviolet Degradation and Stabilization of Plastics, S.P.E. Transactions 2, #1 (1962).

6. Stephenson, C.V. et al, Ultraviolet Irradiation of Plastics III Decomposition Products and Mechanisms, J. Poly. Sci. 55, 477 (1961).

7. Sharkey, W.H. and Mochel, W.E., Mechanism of the Photooxidation of Amides, Journal Am. Chem. Soc. 81, 3000 (1959).

8. Moore, F.R., The Photo Chemical Degradation of Polyamides and Related Model N-Alkylamides, Polymer 4, 493-513 (1963).

9. Ford, R.A., Photochemical Processes in Solids: The Kinetics of Free Radical Reactions in Nylon, J. Colloid Sci. 12, 271 (1957).

10. Achhammer, B.G., Reinhart, F.W., and Kline, G.M., Mechanism of The Degradation of Polyamides, J. Res. N.B.S., 46, 391 (1951).

11. Hasselstrom, H.W. et al, The Behavior of Nylon Oxford Cloth"41" on Pyrolysis, Text. Res. Journal 22, 742 (1952).

12. Liguori, A.M. et al, Ultraviolet Absorption Spectra of Polyamides, J. Poly. Sci. 10, 510 (1953).

PRECEDING PAGE BLANK

13. Yelland, W.E.C., Deterioration Problems in Organic Fibers, Materials for Parachute and Retardation Devices, M.I.T. Summer Session (1959).

14. Beste, L.F. and Houtz, R.C., Amide Interchange Reactions, J. Poly. Sci. $\underline{8}$, 395 (1952).

15. Lindenmeyer, P.H., J. Polymer Sci., C-1, 5 (1963).

16. Geil, P.H., Chapter 1 — Fracture Processes in Polymeric Solids, B. Rosen,Ed., Wiley, New York (1964).

17. Peters, R.H., Textile Chemistry, Volume I, Elsevier, New York (1963).

18. Kieth, H.D., Physics and Chemistry of the Organic Solid State, D. Fox, M.M. Labes and A. Weissberger, Eds., Wiley, New York (1963).

19. Kieth, H.D., F.J. Padden, Jr., and R.G. Vadinsky, J. Polymer Sci., $\underline{a-2}$, 267 (1966).

20. Anderson, F.R., J. Polymer Sci., $\underline{C-8}$, 275 (1965).

21. Peterlin, A., J. Polymer Sci., $\underline{C-9}$, 61 (1965).

22. Peterlin, A., Kollo' Z, $\underline{216}$, 179 (1967).

23. Desmore, R.F., and Statton, W.O., J. Polymer Sci., $\underline{C-13}$, 133 (1966).

24. Bueche, F., Rubber Chem. Technol. $\underline{32}$, 1263 (1959).

25. Geil, P.H., Chapter IV — Fracture Processes in Polymeric Solids, B. Rosen,Ed., Wiley, New York (1964).

26. Starkweather, H.W., C.E. Moore, J.E. Hansen, T.M. Roden, R.E. Brooks, J. Polymer Sci., $\underline{21}$, 189 (1956).

27. Illers, K.H., H.G. Kilian, and E.R. Rosfield, Am. Rev. Phys. Chem. $\underline{12}$ (1961).

28. McCall, D.W. and Anderson, E.W., Polymer $\underline{4}$, 93 (1963).

29. Starkweather, Jr., H.W., J. Polymer Sci. 2, 129 (1959).

30. Boukal, I., J. Appl. Polymer Sci. 2, 1483 (1957).

31. Tsuruta, M. and A. Koshimo, J. Appl. Polymer Sci. 2, 39 (1965).

BIBLIOGRAPHY

Barghoorn, Elso S., Studies on the Deterioration of Textiles unde Tropical Conditions in the Canal Zone, U.S. Office of Scientific Research and Development, Report 4807, April 1945.

India, Exposure Trial on Nylon Cordage, Technical Development Establishment, Technical Report Bio/49/72, June 1949.

Miles, T.D., Climatic and Seasonal Effects in the Weathering of Cotton, Nylon, and Acetate, U.S. Army Quartermaster Research and Development Laboratories, Textile and Leather Division, Textile Functional Finishes Lab Report No. 112 (1954).

Swallow, J.E., The Deterioration of Nylon by Weathering, R.A.E. (Royal Aircraft Establishment) G.B. Technical Note No. Chem. 1389, 1962.

Swallow, J.E., Baldock, F.A., and Webb, M.W., 'Weathering of Fiberous Nylon and Assessment of Some Protective Treatments, Technical Report #64081, Royal Aircraft Establishment, Dec. 1964.

Chakravarti, B.M., Study of the Behaviour of Nylon Sheathed Outdoor Cables for Use in Tropical Climates, Electronics Research and Development Est., High Grounds, Bangore, India.

Leininger, R.I., Hamilton, C.W., and Sommerman, G.M.C., Natural and Artificial Ageing of Wire Jackets," Wire and Wire Products, Feb. 1956, 31 #2 187(1956).

Weiner, L.I., and Sheehan, L.J., Extent and Cause of Deterioration of Nylon Mountain Climbing Rope, Clothing and Organic Materials Division, U.S. Army Natick Labs., Technical Report 66-24-CM (1966).

45

Bayley, C.H., Tweedie, A.S., and Mitton, M.T., Cause of Damage in Nylon Canopies of T-10 Reserve Parachutes, Textile Chemistry Section, Division of Applied Chemistry, National Research Council of Canada, Special Report C98-635.

Bayley, C.H., Mitton, M.T., and Sturgeon, P.Z., An Assessment of Factors Relating to the Actinic Degradation of Automobile Seat Belts, Textile Chemistry Section, Division of Applied Chemistry, National Research Council of Canada; Special Report C410-655 (1965).

Muse, J.W., Evaluation of Nylon Parachute Fabric After Exposure to Artificial Sunlight," WADC Technical Note WCRT 53-233, December 1953 (Wright Air Development Division).

Richards, H.R. and Frank, G.C., "Effects of Radiation on Textile Fibers," Eighth Commonwealth Defence Conference on Clothing and General Stores, Australia (1965).

Wilcox, W.C. et al, "Deterioration of Textile Materials by UV Light," PB 171417 from O.T.S., U.S. Department of Commerce, Washington, D.C.

Yelland, W.E.C. and Cowie, W.A., "Anomalous Behavior of Nylon Parachute Webbing Caused by Exposure to Solar Radiation, Clothing and Organic Materials Division, U.S. Army Natick Labs., Textile Engineering Laboratory Report.

Powers, W.J., Effect of Outdoor Weathering on Plastics, Plastics and Packaging Laboratory, Picatinny Arsenal, Dover, New Jersey.

Moseley, Jr., J., Effect of Internal Structure and Local Defects on Fiber Strength, J. Appl. Poly Sci 7 #1 187-201 (1963).

Tsuruta, M., Koshimo, A., and Tagawa, T., Steam and Heat Setting of Nylon 6 Fiber III. Changes in Viscosity and Amino and Carboxyl End Groups by Heat Setting, J. Appl. Poly Sci 9 #1 25 (1965).

Boyd, R., Dielectric Studies on 6,6 Nylon, J. Chem. Phys 30 1276 (1959).

McCall, "Dielectric Studies on 6 Different Polyamides, J. Chem. Phys 32, 237 (1960).

Use of Uv Light as a Visual Means for Detecting Acid Damage of Nylon and Dacron, WADD Technical Report 60-584.

Tsuruta, M. and Koshimo, A., Steam and Heat Setting of Nylon 6 Fiber V. Invest. of Wide and Small - Angle X-ray Diffraction, J. Appl. Poly Sci 9 #1 39 (1965).

Correlation of Molecular Orientation Measurements in Fibers by Optical Birefringence and Pulse Velocity Methods, Text. Res. Jr., Vol 32 #10 866 (1962).

Moseley, Jr., W.W., The Measurement of Molecular Orientation in Fibers by Acoustic Methods, J. Appl Poly Sci 3, #9, 266-276 (1960).

Charch, W.H., Moseley, Jr., W.W., Structure Property Relationships in Synthetic Fibers, Part I Structure as Revealed by Sonic Observation, Text Res. Jr., 29, No. 7 525 (1959).

Koshimo A. and Tagawa, T., Investigation of Fine Structure of High Polymers by the Method of Deuterium Exchange, I. Changes in Lateral-Order Distribution of Nylon 6 by Heat Setting, J. Appl. Poly. Sci 9 #1 117 (1965).

Woodward, Crissman, and Sauer, Investigations of the Dynamic Mechanical Properties of Some Polyamides, J. Poly. Sci 44, 23 (1960).

Quistwater, J.M.R. and Dunell, B.A., Dynamic Mechanical Properties of Nylon 66 and the Plasticizing Effect of Water Vapor on Nylon II, J. Appl. Poly Sci 1 267 (1959).

Kawaguchi, T., The Dynamic Mechanical Properties of Nylons, J. Appl. Poly Sci 2, 56 (1959).

Dunell, B.A., Joanes, A.A., and Rye, R.T.B., Viscoelastic Behavior of Nylon 6-6 Monofilaments Below Room Temperature, J. Colloid Sci 15, 193 (1960).

Dunell, B.A. and Quistwater, J.M.R., Effect of Humidity on the Dynamic Moduli of Nylon 6-6 Monofilaments, J. Chem. Phys 29 450 (1958).

Hammerle, W.G., Montgomery, D.J., Stress Relaxation of Nylon 66 by Torsional Twisting. Text Res. Jr. 23, 595 (1953).

Fujino, K., Kawai, H., Horino, T., and Miyamoto, K., Exp. Study of the Viscoelastic Properties of Textile Fibers, Part II: Influence of Physical Treatments Upon the Dynamic Properties of Some Fiber Forming Polymers, Text. Res. Jr. 26, 852 (1956).

Catsiff, E., Alfrey, T., and O'Shaughnessy, M.T., Generalized Creep Curves for Nylon, Textile Research Jr. 23, 808 (1953).

Tsuruta, M. and Koshimo, A., Steam and Heat Setting of Nylon 6 Fiber I. Effect of Dry Heat Setting and Steam Setting on Young's Modulus and Specific Gravity of Nylon 6 Fiber, J. Applied Poly. Sci. 9 #1,3 (1965).

Illers, K.H., Lilian, H.G., and Kosfield, R., Physical Properties of High Polymers (Polyamides), Am. Rev. of Phys. Chem., 12 55 (1961).

Biggs, Nylon Deterioration, Bell System Technical J. 30 1078 (1951).

Kuznetsova and G.O. Tatevos'yan Plastckeskie Massy, Changes in Properties of a Polyamide Film on Irradiation, (9) 32-7 cf. C.A. 58 1639h, (1964).

Stephenson, C.V. et al., Ultraviolet Irradiation of Plastics II. Crosslinking and Scission, J. Poly. Sci. 55 465 (1961).

Stephenson, C.V., Moses, B.C., and Wilcox, W.S., Ultraviolet Irradiation of Plastics I. Degradation of Physical Properties, J. Poly. Sci. 55 451 (1961).

Stephenson, C.V. and Wilcox, W.S., Ultraviolet Irradiation of Plastics IV Further Studies of Environmental Effects on Films and Fibers, J. Poly. Sci. Part A. 1 2741 (1963).

Foerster, Bochmaier, huszik, and Seidel, Polyamide Deterioration by Light, Karrosion 16 11-12 (1964).

Rafikov, S.F. and Shik-P'ing Hsu, Chemical Change in Polymers: VI The Effect of UV Irradiation on Polyamides in Presence of Oxygen and Water Vapor, Vysokomolekul Soedin 4 851-9 (1962).

Rafikov and Tzu -P'ing Hsu, Chemical Change in Polymers: V Photo Chemical Transformation of Polycaproamide in Vacuum Under the Influence of Uv Light, Vysokomolekulyarnnye Soedineniya 3 56-65 (1961).

Egerton, G.S. and Shah, K.M., Effect of Temperature on the Photosensitized Degradation of Textile Fibers, Nature 202 (4927) 81-2 (1964).

Bayley, C.H., Mitton, M.T., and Sturgeon, P.Z., An Assessment of Factors Relating to the Actinic Degradation of Automobile Seat Belts, Textile Chemistry Section, Division of Applied Chemistry, National Research Council of Canada, Special Report C410-655 (1965).

Bovey, F.A., The Effect of Ionizing Radiation on Natural and Synthetic High Polymers, Interscience (1958).

Little, K., Some Effects of Irradiation on Nylon and Polyethylene Terephthalate, Nature 173 680 (1954).

Burrell, E.J., Jr., 'Formation and Identification of Unique Radical Sites in Irradiated Amides, Jr. Am. Chem. Soc. 83 574 (1961).

Rao, P.S., Rogers, M.T., and Bolte, S., "Electron Paramagnetic Resonance Study of Radicals Produced in Irradiated Amides," Jr. Am. Chem. Soc. 87 1875 (1965).

Rader, C.A. and Schwartz, A.M., Accelerated Deterioration of Textiles, Contract: Harris Research Labs. Inc. #DA18-108-CML-6606 (1963).

Mikolayewski, Wet Oxidation of Undrawn Nylon 6-6 and Model Amides, J. Appl. Polym. Sci 8 2067-2093 (1964).

Meyer and Gearhart, Photo Oxidation of Nylon and Cellulose Esters, Ind. and Eng. Chem. 37 232 (1945).

Rochas, P. and Martin, J.C., Study of the Stability to Heat of Polyamide 66, Bull- de l'Institu Textile de France, #83 41-84 (1959).

Lis, S.J., Engholm, G., and Bambenek, R.A., Thermal Conductivity of Nylon Parachute Fabrics Subjected to Compressional Stresses, Textile Res. J. 32 (1) 24-8 (1962).

Roth, W. and Schroth, R., Effect of Heat and Light on the Stability of Polyamides I. Influence of Thermal and Hydrothermal Treatments, K.L. Chem. Geol. Biol. (1) 285-92, (1963).

Coplan, M., A Study of the Effect of Temperature on Textile Materials, (Fabric Research Laboratories), WADC Tech. Report 53-21 (March 1953).

Rogavina, A.A., Novikova, S.A., Gil'man, I.S., and Vasilieu, Y.U., Nature of the Fatigue of Tire Cord, Khim. Volokna (4) 56-60 (1964) ibid (4) 63-8, (1962).

Surnita, M., Koshimo, A., and Tagawa, T., Steam and Heat Setting of Nylon 6 Fiber IV - Relationship Between Heat Setting and Swelling, J. Appl Poly Sci 9 #1 31 (1965).

Powers, W.J., Effect of Outdoor Weathering on Plastics, Plastics and Packaging Lab., Picatinny Arsenal, Dover, New Jersey.

Singleton, R.W., Kunkel, R.K., and Sprague, B.S., Factors Influencing the Evaluation of Actinic Degradation of Fibers, Text. Res. Jr. 35#3 228 (1965).

Bretislov, Dolezel, Technique of Accelerated Ageing Tests of Plastics, Chem. Prumysl 13 7 388-91 (1963).

Koshimo, A., Steam and Heat Setting of Nylon 6 Fiber VII I R Spectra of Nylon 6 Prep. from N-Deuterated and Caprolactam and the Water Accessibility of Nylon 6 in Steam Setting, J. Appl. Poly Sci 9 1 55 (1965).

Koshimo, A., and Tagawa, T., Steam and Heat Setting of Nylon 6 Fiber VI Water Adsorption on Nylon 6 Fiber, J. Appl. Poly Sci. 9 #1 45 (1965).

Hoshimo, K. and Yamoto, H., Sorbed Water is a Function of Temperature and Relative Humidity for Nylon 6, J. Chem. Soc. Japan 70 104 (1949).

Starkweather, H.W., Clustering of Water in Polymers, Polymer Letters 1 133 (1963).

Starkweather, H.W., Jr., The Sorption of Water by Nylons, J. Appl. Poly. Sci. 2 129 (1959).

Quistwater, T., 'Dynamic Mechanical Properties of Nylon 66 and the Plasticizing Effect of Water Vapor on Nylon 66, J. Poly. Sci. 28 309 (1958).

Glick, Proton Magnetic Resonance of Polyhexamethylene Adipamide, J. Poly. Sci. 42 271 (1960).

Bobalek, Mechanical Properties of 6,6 6,10, and 6 Nylon in Process with Steam and Heat, J. Appl. Poly. Sci. 3 113 (1960).

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
U.S. Army Natick Laboratories Natick, Massachusetts 01760	UNCLASSIFIED
	2b. GROUP

3. REPORT TITLE

STRENGTH LOSSES IN NYLON PARACHUTE MATERIALS WITH TIME, EXPOSURE AND USE

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Summary and interpretation of studies completed in 1967

5. AUTHOR(S) (First name, middle initial, last name)

Frank Figucia, Jr. and Richard D. Wells

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
March 1968	60	14

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. Applications Engineering Proj.1 Task 01; Safe Life Span of	68-45-CM
c. Personnel Parachutes in Service and Storage	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) TS-156
d.	

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale;
its distribution is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	U.S. Army Natick Laboratories Natick, Massachusetts 01760

13. ABSTRACT

The findings of recent U. S. Army Natick Laboratories tests on aged and used nylon parachutes are reviewed with respect to service life limits and to implications as to the technical nature of the degradation problem. The data tend to confirm that the current 10 year or 100 jump limits and related repair cost limit schedules do not present a hazard. However, the scatter and contrasts of results make questionable the validity of small samplings and extended predictions. No consistent and pervasive trends were found to be directly related to time in storage or service, or to jump history except for initial mechanical effects on suspension lines. The results evidenced marked differences in the specific susceptibilities of various materials, and a number of degrading influences and types of effects on physical properties.

It is concluded that a wide distribution of strength levels is to be expected in older parachute populations, and that the risk problem is with the exceptional cases rather than with the average condition. A number of possible chemical and structural change mechanisms are discussed.

DD FORM 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

UNCLASSIFIED
Security Classification

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Strength	8					
Storage changes	8					
Wear, resistance	8					
Nylon	9		7			
Parachutes	9		7			
Storage			6			
Exposure			6			
Parachute jumping			6			